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Friction and Wear Properties of MoS_2 Thin-Film Lubricants

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14. ABSTRACT

The generally agreed upon mechanism for lubrication of sliding and rolling contacts by MoS_2 thin films consists of the movement of crystallites (micro or nanocrystals) over one another with friction determined by the interactive forces between the basal planes of individual crystallites and wear by the eventual loss of material in the contact. It has been proposed that long life can be achieved by the recirculation of crystalline material into the contact area from reservoirs of lubricant (debris) that accumulate outside of the contact. Chemical and structural (morphological) properties of films have been implicated in determining friction and wear behavior, but the relationship between these properties and the intercrystalline slip lubrication mechanism has not been clarified. In this paper we review data on the results of thrust-bearing tests of sputter-deposited films, specifically as they relate to test environment, and attempt to provide a chemistry-based model of lifetime variation. We present new data on lubricant transfer-film formation and the effects of test environment, from which we propose that bearing life is determined by the efficiency of chemical bonding between MoS_2 "debris" and uncoated or worn metal surfaces.

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Solid lubrication, Wear-life model, Molybdenum disulfide, Thrust-bearing tests

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1. Introduction

In a recent paper we compared the friction properties of MoS_2 lubricant films having varying amounts of oxygen substitution within the crystal lattice to those with some degree of oxidation of the Mo(IV).[1] We presented a chemical-mechanical model to describe friction variations of films based on the degree of oxygen substitution in the basal plane of the MoS_2 crystals. Wahl and Singer have proposed that long life in sliding systems is achieved by means of the recirculation of crystalline material into the contact area from reservoirs of lubricant (debris).[2] In this report, we present new data on lubricant transfer-film formation and an interpretation of wear life for thrust-bearing tests conducted in vacuum and under nitrogen gas purge.[3,4] The test life in nitrogen is almost twenty times longer than that in vacuum (<1.3 x 10^{-5} Pa). We will provide a chemistry-based model of transfer film formation, from lubricated raceways to unlubricated balls and retainers, that we believe explains the seemingly anomalous results of these bearing tests. This model draws upon aspects of the Wahl-Singer transfer processes and provides an alternative to a previous explanation of the lifetime data.[4]

2. Experimental

Two types of test were conducted, thrust bearing tests and ultrahigh vacuum (UHV) tribometry. Each apparatus has been described previously.[3,5] The thrust-bearing tester was operated under high vacuum conditions, base pressure <1.3 x 10^{-5} Pa, or with flowing gases at atmospheric pressure (~100 kPa). Bearings were tested under a 30-pound load, producing a mean Hertz stress of 75 ksi, approximately 0.5 GPa. The bearings were operated unidirectionally at 2500 rpm until failure, which was determined from a rapid rise in torque of a factor of five to ten. Some bearing tests were stopped (interrupted) after a fraction (~20-30%) of life in order to examine the properties of the lubricant transfer films. The compositions and relative thicknesses of lubricant films, including the films transferred to the balls, were examined in the x-ray photoelectron spectrometer (XPS).[1]

The UHV tribometer consists of a pin-on-disk apparatus with the capability of conducting x-ray photoelectron spectroscopy of the pin and/or disk surfaces, upon interruption of the test, while maintaining the specimens under UHV conditions. A schematic diagram of this test apparatus is shown in Figure 1. The "pins" consist of 3/16" 440C steel balls. The load on the pin was 0.6 N and the rotational speed of the 440C-steel disk was 120 rpm, with the diameter of the pin track being 1 cm. Tests in this tribometer were also conducted with variable pressures of residual gases in the chamber or under flowing gas at atmospheric pressure.

Lubricant films for bearing tests were prepared in-house (Aerospace – AT films) by rf sputter deposition.[3] Thrust bearing raceways were coated to a nominal thickness of 1 µm, but balls and retainers were not coated. The retainers were of the stamped metal type with no active lubrication. Disks for the UHV tribometer were either fully coated (on the entire wear surface), or they were masked so that only half of the disk was coated with MoS_2 to evaluate the properties of lubricant-transfer films on the uncoated pins (balls) or the uncoated portions of the disks.[5] A new multiple-target deposition facility was used to prepare films for the UHV tribometer experiments. A single MoS_2 target was used under conditions that produce AT-type films with 2 to 3 at % oxygen substitution. The vacuum chamber for this facility has a base pressure of ~3 x 10^{-7} Pa and a load-lock mechanism for substrate entry and removal. As-deposited films had various quantities of substitutional oxygen, but in general the amount was not specifically analyzed. For most film batches the degree of oxidation, crystallinity, and morphology were determined, but not necessarily on the specimens tested.

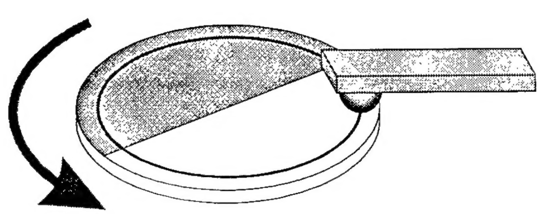

Figure 1. Schematic diagram of UHV test.

3. Results and Discussion

Typical torque traces for thrust bearing tests are shown in Figure 2. Lifetimes under nitrogen purge, were 3 to 3.5 million cycles, while those under high vacuum were approximately 180,000 cycles, even though the latter ran with lower torque, presumably because of the absence of windage effects. The trends in measured torque are the same for all tests, with an initial, run-in period of decreasing torque and a rather sudden failure preceded by some noise episodes. During the tests, lubricant was transferred from the raceways to the balls and then to the retainers. The interrupted tests (after 20 to 30% of total life) showed that most (~70-80%) of the film was removed from the wear track of the initially coated receways during the early run-in period. The balls and retainers from these early observations contained more uniform transfer-film formation with more overall film, especially at the ball-retainer interface, for the nitrogen tests than for the vacuum tests. For the interrupted tests XPS results showed two-times more MoS_2 species on the balls for the nitrogen tests than on those from the vacuum tests. Some tests were conducted with an initial run in the N_2 environment (50,000 revolutions) followed by operation in vacuum. This attempt to produce lubricant transfer films did not result in significantly increased operating life over the results for complete operation in vacuum. (Figure 3).

The transfer films for the N_2 tests exhibited a greater sulfur deficiency (Table 1) with some Mo in a higher oxidation state than for the vacuum tests, especially for the interrupted tests but also for the tests run to failure. Lubricant debris was scattered throughout the entire vacuum chamber after the vacuum tests but was confined to the bearing parts after the N_2 tests. Figure 3 also shows results for tests conducted under He and CO_2 atmospheres. One of the He tests lasted almost as long as the average N_2 test, but those under CO_2 were only slightly better than for the vacuum conditions. The degree of sulfur deficiency in the films for the He tests was much like those in the vacuum tests and again less than for the tests under N_2. Films tested under CO_2 showed high levels of Mo oxidation compared with the other environments. Finally, a set of bearing tests with the chamber filled to intermediate pressures of N_2 was conducted with the combined results shown in Figure 4. In these

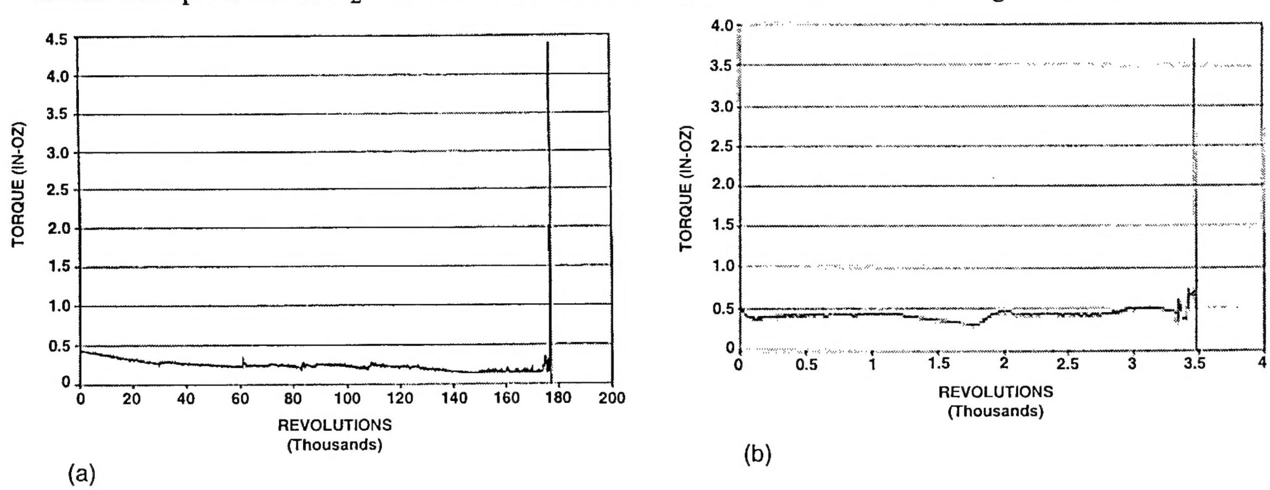

Figure 2. Torque trace for test run (a) in vacuum and (b) in dry N_2.

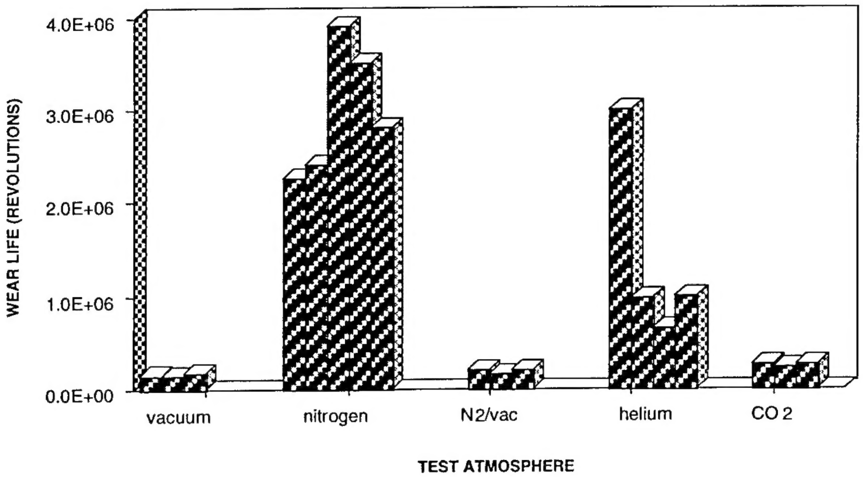

Figure 3. Wear life results for thrust-bearing tests conducted in different environments.

Table 1. XPS Results for MoS_x Films on Balls

	% Mo	% S
Interrupted Tests		
N_2 test	15	16
Vacuum	7	11
Run to Failure		
N_2 test	9-11	16-17
Vacuum	6-7	11-13

Note: Remaining material is composed of carbon, oxygen, and substrate elements

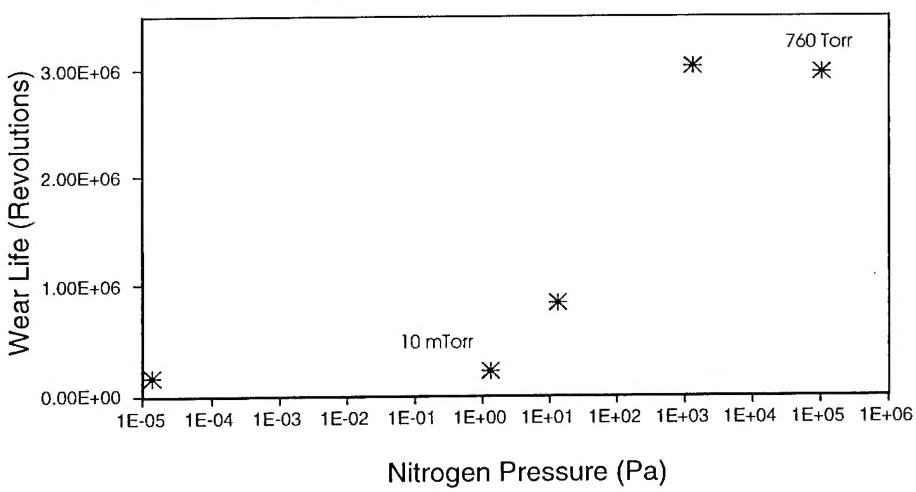

Figure 4. Thrust-bearing wear life vs. nitrogen pressure

tests, there is evidence for a threshold pressure at which the bearing life rises dramatically to a plateau value. Although more data points are needed to determine the actual shape of this curve, it is reminiscent of the shape of an adsorption isotherm, where all surface sites become occupied at a particular pressure and the amount of gas adsorbed to the surface reaches a maximum.

These results suggest that a chemical interaction of a gas in the test atmosphere is the cause of enhanced performance. We believe that this chemical influence may be positive or negative, depending on whether it induces bonding of the MoS_2 to the uncoated surfaces (including wear surfaces) or it causes oxidation of the MoS_2. The former condition enhances life, while the latter leads to premature failure. In order to investigate the nature of the bonding process(es) of transferred, lubricant films we conducted a series of UHV, pin-on-disk, tribometry measurements of half coated disks. These measurements provide an evaluation of the efficiency of transfer-film formation under different environmental conditions (e.g., vacuum versus N_2). The results of these tests are shown in Figure 5, wherein the coefficient of friction (COF) is plotted as a function of the number of revolutions of the disk. The pin travels from coated surface to uncoated surface throughout the course of one disk revolution, and the COF oscillates from a low value (~0.03) to a very high value (~1), in a corresponding fashion. The data of Figure 5 show that depending on the test environment, the COF is either reduced rapidly on the uncoated half of the disk, indicating very efficient transfer of lubricant, or it remains high and erratic, indicating inefficient transfer. Figure 5a shows that the transfer film under one atmosphere of N_2 forms within 200 revolutions and that the subsequent COF is quite stable. In contrast, Figure 5b shows that under high vacuum the transfer film is not formed until more than three times the number of revolutions and that even when the COF is reduced it still exhibits a fluctuation more than two-times that of the N_2 case.

Our belief was that the increased thrust-bearing life and the more efficient lubricant transfer-film formation are related and that they are both due to the effects of an oxygen containing species in the test environment of the N_2. With this in mind and knowing that the N_2 purity level was believed to be better than one part per million, we conducted the pin-on-disk test in an atmosphere of $\sim 1 \times 10^{-1}$ Pa of H_2O (equivalent to 1 ppm). It was our expectation that behavior very similar to that for N_2 would be observed. Figure 6a shows that this was <u>not</u> the case. In fact the behavior under this pressure of water vapor was much worse than that under high vacuum.

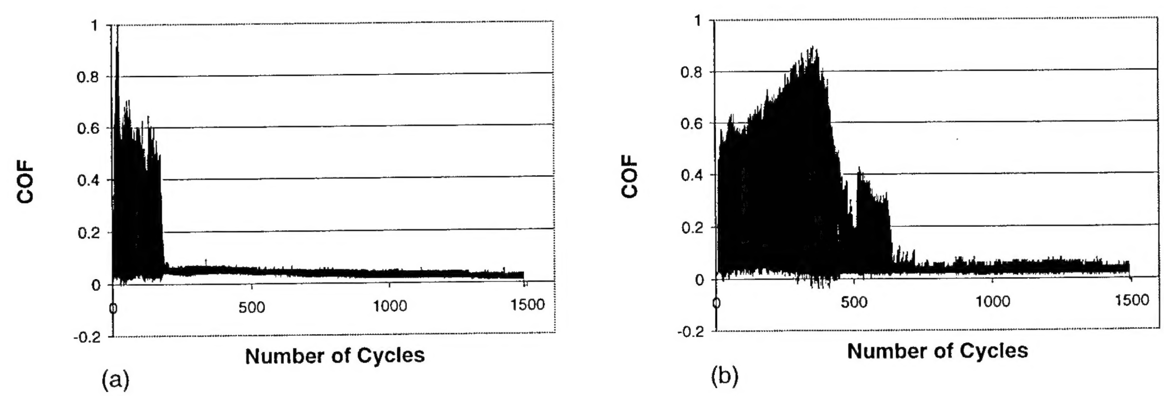

Figure 5. Coefficient of friction (a) vs number of cycles under N_2 and (b) for $\sim 1.33 \times 10^{-6}$ Pa vacuum.

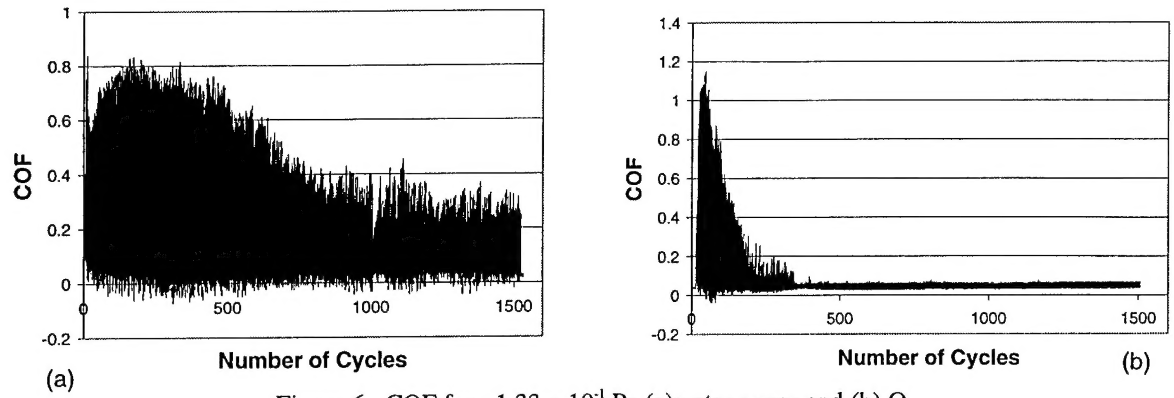

Figure 6. COF for ~1.33 x 10^{-1} Pa (a)water vapor and (b) O_2.

In contrast, Figure 6b shows behavior almost identical to that for N_2 when the test environment was ~1 x 10^{-1} Pa O_2. Again, the transfer film is formed within approximately 200 to 300 cycles and the subsequent COF is low and very stable. We do not have a detailed chemical analysis of the N_2 gas that we use for our experiments, but an uncalibrated mass-spectral analysis indicates that the water content is very low and that there is a measurable amount of oxygen (O_2), well in excess of 1ppm. This N_2 gas is obtained from the "boil-off" from a liquid N_2 tank.

Lifetimes for solid-lubricated bearings depend on keeping lubricant in the contact regions of the balls, races, and retainers. According to the Wahl-Singer model, lubricant debris can be recaptured by the contacting surfaces to provide continuous lubrication. For the tests described here (both bearing and UHV tribometer) it is necessary for lubricant to be transferred from an initial, coated surface to one uncoated surface (ball or pin) and then to a second uncoated surface (retainer or disk). The efficiency of these transfer processes and the uniformity of the transfer films in other sliding wear tests have been determined to be a function of the composition of the initially deposited film.[6] Some degree of surface oxygenation or oxidation of the MoS_2 coating provides for much more uniform and continuous transfer films. The tests reported here show that in a flowing N_2 environment or a static partial pressure of O_2 more transfer of more uniform films occurs than for tests in high vacuum.

It might be argued that long life in the bearing tests could be achieved by precoating the balls and retainers in addition to the receways. Indeed, this procedure would probably increase life to some limited extent, but as shown in the interrupted bearing tests, up to 80% of the initial coating is removed from the wear track very early in life. Presumably, similar amounts of coating would be worn off of precoated balls, and long life would still depend on the recirculation and bonding of the lubricant debris to the wear tracks on the receways and balls. The tests in which the bearings were run in N_2 for 50,000 cycles and then in vacuum, that showed little increase in life, would tend to support this argument. Some material should have been transferred during the run-in, but since there was no continuous supply of bonding agent to promote adhesion of material to the balls, retainers, or worn receways, the bearings failed during the vacuum portion of the run.

4. Summary and Conclusions

We submit that the reason that the bearing tests conducted in flowing N_2 have such longer lifetimes than those done in high vacuum is because the transfer films form more efficiently in the former, and these films are continuously reformed by means of recirculation of the debris generated during the tests. We also submit that the reason the transfer films form more effectively in N_2 is that there is a continuous supply of oxygen in the N_2 that makes bonding to counter surfaces more effective, probably as a result of oxygen bridge bonding between Mo and Fe through oxygen substitution in the MoS_2. In high vacuum there is insufficient oxygen to collide with the contacting surfaces to provide efficient oxygen-substitution-induced bonding of the transferring material. Bearing tests conducted in the CO_2 atmosphere and pin-on-disk tests conducted in 1×10^{-1} Pa H_2O show that oxidation of the MoS_2 does not provide long bearing life or good lubricant transfer films. Apparently, only conditions that promote bonding between the film and the substrate surface lead to longer wear life by enhancing the recirculation phenomenon proposed by Wahl and Singer. Additional proof of our hypothesis concerning the environmental effects on wear life of bearing tests will come from planned operation of the bearings in dry O_2 at low pressure.

References

1. P. D. Fleischauer and J. R. Lince, "A comparison of oxidation and oxygen substitution in MoS_2 solid film lubricants," *Tribol. Int.*, **32** (1999) 627-636.

2. K. J. Wahl and I. L. Singer, "Quantification of a lubricant transfer process that enhances the sliding life of a MoS_2 coating," *Tribol. Letters* **1** (1) (1995) 59-66.

3. S. V. Didziulis, M. R. Hilton, R. Bauer, and P. D. Fleischauer, "Thrust Bearing Wear Life and Torque Tests of Sputter-Deposited MoS_2 Films," Aerospace Report No. TOR-92(2064)-1, 15 October 1992.

4. M. N. Gardos, "Anomalous wear behavior of MoS_2 films in moderate vacuum and dry nitrogen," *Tribol. Letters* **1** (1) (1995) 67-85.

5. P. P. Frantz and S. V.Didziulis, "Measurement of Friction Coefficients between Oxidized and Contaminated Surfaces in Vacuum and in Air," *Proc. 34 Aerospace Mechanisms Symposium*, NASA/CP—2000-209895, May 2000.

6. P. D. Fleischauer and R. Bauer, "Chemical and Structural Effects on the Lubrication Properties of Sputtered MoS_2 Films," *Tribol. Trans.* **31** (2) (1988) 239-250.

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